

Appl. No. : 09/787,062
Filed : June 28, 2001

REMARKS

Phone Interview

Applicants thank the Examiner for extending the courtesy of a phone interview on September 16, 2003 during which Applicants' representatives, Adeel Akhtar and Demian Jackson, discussed with the Examiner the relevance of the skilled artisan's understanding of ALE to the cited art, but could not reach an agreement.

In particular, during the Interview, the Examiner continued to assert that DiMeo's teaching of 5 Å layers being deposited per cycle meets Applicants' recitation of atomic layer epitaxy. Applicants disagreed with this interpretation of the claims for two reasons. First, Applicants recite "Atomic Layer Epitaxy," which is a well-recognized term of art that excludes DiMeo's CVD process teaching of simultaneous provision of mutually reactive vapor reactants. Second, Applicants recited alternate, *self*-limiting surface reactions, while DiMeo is externally *mechanically* limited.

Additionally, the Examiner continued to assert that DiMeo's single Background reference to ALD can be combined with the digital CVD method of the Detailed Description, a combination for which no suggestion has been provided.

Claim Rejections

In the most recent Office Action, the Examiner has continued to reject all pending claims as unpatentable over DiMeo (U.S. Patent No. 5,972,430) in view of Kirlin (U.S. Patent No. 5,453,494) and/or Maita (U.S. Patent No. 6,020,024). In response, Applicants argue that the Examiner has continued to misunderstand that atomic layer epitaxy (ALE) is a term of art which does not encompass the prior art CVD processes regardless of whether or not those CVD processes are alternated or "digital" CVD processes. In addition, Applicants assert that, even if the Examiner can show that the art of record teaches ALE in general, the references, when combined, do not suggest ALE deposition using one of Applicants' recited cyclopentadienyl precursors.

Rejected Claims 1-27 and 36-39 recite a layer produced by "Atomic Layer Epitaxy (ALE)" using a recited cyclopentadienyl precursor, the ALE method providing alternate "self-limiting surface reactions on the substrate." In addition, Claims 28-35 have been amended to

Appl. No. : 09/787,062
Filed : June 28, 2001

recite “self-limiting Atomic Layer Epitaxy (ALE).” Accordingly, all pending claims recite “self limiting” reactions by “ALE” employing an cyclopentadienyl precursor.

In the most recent Office Action, Applicants respectfully submit that the Examiner continues to evidence a fundamental misunderstanding as to what ALE (otherwise known as ALD) encompasses to the skilled artisan. For example, the Examiner argues that self-limited ALE is taught in Maita by citing the reference’s formation of “one atomic layer at a time” using “nanolaminate processing.” Col. 3, ll. 55-63. Based only on this ability to form atomic layers, the Examiner summarily concludes that “Maita et al. discloses that such CVD can have the individual reactants flowed in to form *atomic layers (i.e. self limited thickness)*.” Office Action at p. 4. (*Emphasis Added*). This is a faulty assumption. It does not follow that, just because a given deposition method is capable of forming an atomic layer, the method is, therefore, inherently self-limited. Likewise, the Examiner’s assertion that DiMeo teaches ALE because the reference “teaches about *5 angstrom thick layers* which in turn *suggest an atomic layer process*” is similarly incorrect. Office Action at p. 7 (*Emphasis Added*). The skilled artisan, would not conclude that any method capable of being manipulated to form atomic layers is *self*-limited ALE, when DiMeo expressly teaches processes that are *mechanically limited* by timing the valves. In the absence of this mechanical control, DiMeo’s CVD process would otherwise continue deposition indefinitely. While DiMeo’s process is “limited,” it is externally limited and therefore not “self-limiting” by surface reactions.

ALE (otherwise known as ALD) is a term of art which, as the skilled artisan would recognize, does not encompass CVD. Instead, the skilled artisan would understand that ALE, unlike CVD, involves depositing a layer upon a substrate through alternating, self-limited surface reactions. Applicants respectfully direct the Examiner to the enclosed Bedair article evidencing an example of the skilled artisan’s understanding of ALE (as compared with CVD), an excerpt of which follows:

In *contrast* to MBE [molecular beam epitaxy] and MOCVD [metal organic chemical vapor deposition] growth, in which reacting precursors are introduced *simultaneously* and reach the substrate surface together, ALE growth of III-V compounds, for example, proceeds by exposing the substrate surfaces to group III precursors in the *absence* of group V precursors, followed by exposing the substrate surface of group V precursors in the *absence* of group III precursors. Accordingly, the *basic principle of ALE growth* is based on *alternating* chemisorption, surface reaction, and desorption of the reactants. ALE growth is characterized by its *self-limiting* deposition process...[and] ALE growth promises extremely uniform thickness and very

Appl. No. : 09/787,062
Filed : June 28, 2001

good growth reproducibility...[, t]hese are *difficult to achieve by conventional growth methods* where all the reacting species are *mixed together* on top of the substrate.”

Bedair, S.M., “Atomic layer epitaxy deposition processes,” Journal of Vacuum Science Technology B, 12 (1), pp. 179-185, 179 (Jan/Feb 1994)(*Emphasis Added*).

ALE deposition is inherently self-limited in that, once the substrate surface is saturated with a given reactant, deposition effectively ends and no more of that reactant will adsorb *regardless of the amount* of that reactant flowed across the substrate. As a result, all that is required to deposit an atomic layer of a reactant is to ensure precursor is injected at or greater than the amount needed to saturate the substrate surface, *i.e.*, overshooting the saturation point does not affect the deposition thickness. In other words, ALE automatically effectuates a highly precise deposition without necessitating precise mechanical control over reactant supplies. In contrast, the thickness of a layer deposited by CVD is *not self-limiting* (even if it results in one atomic layer being deposited), but rather is *always supply dependent*, *i.e.*, thickness is controlled via injection and/or pulse duration and a thick layer can be deposited in bulk with a single pulse. Accordingly, contrary to the Examiner’s conclusions, CVD is neither “an equivalent variant to the related ALE....method,” nor is it correct to conclude that a CVD method is self-limited just because it can be manipulated to form an atomic layer. Office Action at p. 2 and 4.

In view of the above, it is clear that the secondary references do not teach or suggest self-limited ALE at all, much less the ALE deposition of a cyclopentadienyl precursor, as recited by Applicants. The only reference relied on by the Examiner which even mentions ALE is a single passage from DiMeo’s *Background section*. Based solely on this single passage, the Examiner argues that “DiMeo et. al. [at] col. 1[,] lines 43-60 discloses that ALE is a form of CVD deposition useful of multi-component oxide deposition.” Office Action at p. 6. On the contrary, this cited portion from DiMeo does *not* teach that ALE is *a form of CVD*, but rather teaches that “[o]f the methods for forming multi-component oxide thin film layers, (CVD) methods and *related* epitaxial deposition methods, such as but not limited to atomic layer epitaxial (ALE) deposition methods, are in turn also presently of substantial interest.” DiMeo, Col. 1, ll. 44-50 (*emphasis added*).

In any event, even if the Examiner’s characterization of the prior art were correct (Applicants maintain that it is not), the Examiner has still failed to show how this Background passage teaches or suggests anything about employing one of Applicants’ recited

Appl. No. : 09/787,062
Filed : June 28, 2001

cyclopentadienyl precursors in an ALE process. It is not enough to merely show that the DiMeo Background passage is in the same document as the digital CVD method. Instead, the Examiner must show a suggestion to combine DiMeo's Background teaching with fundamentally different teachings in DiMeo's Detailed Description. The skilled artisan, when considering this ALE passage in the context of the entire reference, would conclude that DiMeo is entirely focused on describing a variant of a non-self-limited CVD process without even a passing reference to ALE.

Furthermore, the skilled artisan would understand the above-mentioned fundamental differences between CVD and ALE and, as a result, would recognize that the distinction between the choice of precursors for CVD and the choice of precursors for ALE is *not trivial*. The self-limiting operation characteristic of ALE depends, in part, on the choice of reactant and will not work with every reactant. For example, the enclosed Bedair article teaches that "[c]aution must be used in the selection of reacting species since they also determine the detailed ALE process." Bedair at p. 179. The Examiner cannot, without more, just assume that all precursors taught as desirable for CVD are automatically functional in a fundamentally different process, such as ALE. Furthermore, even if the Examiner could show that CVD precursors would work in Applicants' ALE process (which has not been shown), the Examiner must still show the desirability of employing those particular CVD precursors in an ALE process. The Examiner has shown neither functionality nor desirability. As a result, the Examiner has not provided the requisite teaching or suggestion to combine DiMeo's Background ALE passage with the CVD described in the DiMeo's Detailed Description (i.e., incorporated from Kirlin). Accordingly, Applicants submit that Claims 1-39 are in condition for allowance and respectfully request the same.

Applicants have also amended Claim 16 to correct a typographical error. Accordingly, Applicants submit that Claim 16 is in condition for allowance and respectfully request the same.

Appl. No. : 09/787,062
Filed : June 28, 2001

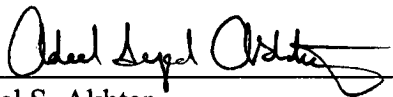
CONCLUSIONS

In view of the foregoing amendments and remarks, Applicants submit that the application is in condition for allowance and respectfully request the same. If, however, some issue remains that the Examiner feels can be addressed by Examiner's amendment, the Examiner is cordially invited to call the undersigned for authorization.

Respectfully submitted,

KNOBBE, MARTENS, OLSON & BEAR, LLP

Dated: September 23, 2003

By: 
Adeel S. Akhtar
Registration No. 41,394
Attorney of Record
2040 Main Street
Fourteenth Floor
Irvine, CA 92614
(415) 954-4114

W:\DOCS\DKJ\DKJ-2846.DOC
091803

S. M. Bedair

Department of Electrical and Computer Engineering, North Carolina State University, Raleigh, North Carolina 27695-7911

(Received 23 March 1993; accepted 20 September 1993)

Atomic layer epitaxy (ALE) is emerging as a promising epitaxial growth technique for thickness control at the atomic level. The article outlines recent progress in ALE of III-V and Si thin films. Also models describing the self-limiting processes will be outlined.

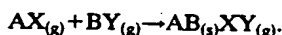
1. INTRODUCTION

Recent progress in epitaxial growth technology has led research in semiconductor materials and devices to a new era. With the advent of the maturity of molecular-beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD), ultrathin semiconductor materials can be prepared routinely. During the past decade, interest has increased rapidly in exploring new physics, chemistry, and materials science of heterostructures. Also novel optical and electrical devices based on quantum size effects have been fabricated, principally in III-V compounds. A new generation of heterostructural devices such as semiconductor lasers, resonant tunneling diodes (RTD), multi-quantum well photo-detectors, and high electron mobility transistors (HEMTs) were designed in accord with the newly developed artificial materials. These structures, however, require precise control in layer thickness and junction abruptness at heterointerfaces. Both MBE and MOCVD have been recognized techniques for the growth of ultrathin epitaxial layers; however, achieving the growth of two-dimensional (2D) heterostructures relies very much on preciseness in the control of growth parameters such as growth temperature, fluxes of source materials, and growth time. Nevertheless, in these two techniques, run-to-run reproducibility for the growth of ultrathin heterostructures becomes difficult due to the inevitable slight variations in growth parameters, which cause growth yield deterioration. Unfortunately, in fabricating 2D heterostructural devices like HEMTs and quantum well lasers, epilayer thickness uniformity and heterointerface abruptness are usually very critical. The demand for easier control of film thickness uniformity and heterojunction abruptness in growing sophisticated heterostructures encourages the resort to a growth process in which growth proceeds in monolayer-by-monolayer fashion.

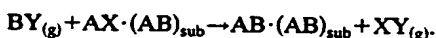
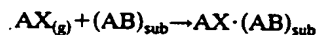
Atomic layer epitaxy (ALE) is a recently developed growth technique which has received much attention because of its unique digital growth process.¹ In contrast to MBE and MOCVD growth, in which reacting precursors are introduced simultaneously and reach the substrate surface together, ALE growth of III-V compounds, for example, proceeds by exposing the substrate surfaces to group III precursors in the absence of group V precursors, followed by exposing the substrate surface to group V precursors in the absence of group III precursors. Accordingly, the basic principle of ALE growth is based on alternating chemisorption, surface reaction, and desorption of the reactants. ALE growth is characterized by its self-limiting deposition

process,¹⁻¹⁰ in which the growth rate is independent of growth parameters such as vapor pressure of the precursors and growth temperature, but is dependent on the number of growth cycles and the lattice constant of the material. ALE also allows epitaxial growth of III-V compounds to proceed at low temperatures. As a consequence, ALE growth promises extremely uniform thickness and very good growth reproducibility of heterointerface abruptness for the grown films. These are difficult to achieve by conventional growth methods where all the reacting species are mixed together on top of the substrate. This growth approach is a potentially powerful growth technique for preparing epitaxial layers for ultrathin film devices.

We will now briefly discuss the mechanism of ALE growth. A general ALE reaction for growing compound AB from reactants AX and BY can be described as



The reaction can be divided into two steps:



In this case, gaseous AX chemisorbs on the compound AB surface, and the oncoming AX, which only weakly physisorbs on the $AX \cdot (AB)_{sub}$, will be removed. When another gaseous reactant BY is introduced, it reacts with the adsorbate AX chemisorbed on the AB substrate surface to form one monolayer of AB, and the gaseous reacting product XY is removed.

Various choices of $AX_{(g)}$ and $BY_{(g)}$ have been utilized for ALE growth. Among them are elements, metalorganics, metal-halides, hydrides, and so forth. Owing to differences in chemical properties between source materials, each individual ALE process may not follow the same reaction route, although the principle of ALE growth looks very straightforward. Consequently, caution must be used in the selection of reacting species since they also determine the detailed ALE process. In general, the greater the difference between the chemisorbed monolayer adsorbate's binding energy on the surface and the subsequent physisorbed species binding energy on the formed monolayers, the better the self-regulating characteristics of the ALE process will be. Because the source materials have to be volatile enough at normal growth temperatures and pressures, metalorganics, which are volatile in nature, are often preferred instead of elemental sources.

ALE growth of GaAs using TMGa and AsH₃ has been achieved in atmospheric MOCVD, low pressure MOCVD,

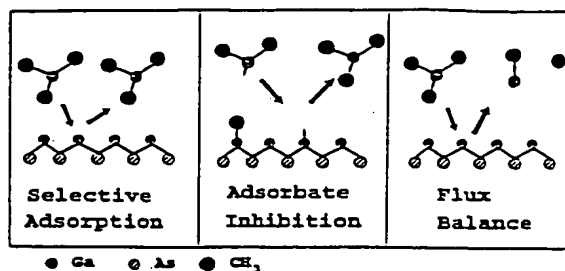


FIG. 1. Summary of three models, of ALE of GaAs using TMGa and AsH₃: selective adsorption allows no TMGa decomposition on a Ga-covered surface. Adsorbate inhibition prohibits TMGa decomposition on a methyl covered surface. The flux balance requires a balance of adsorbing and desorbing methylgallium species.

and chemical-beam epitaxy (CBE) systems. The operating pressures ranged from 760 to 10^{-9} Torr. Nishizawa *et al.*¹⁰ utilized a CBE system for the growth of GaAs by the so-called molecular-layer epitaxy (MLE), in which monolayer deposition was achieved at 500 °C. Bedair *et al.*¹ achieved ALE growth of GaAs in a specially designed reactor and susceptor operated at atmospheric pressure; the self-limiting growth was achieved from 450 to 700 °C. DenBaars *et al.*⁶ also achieved ALE growth at atmospheric pressure using a conventional MOCVD reactor with saturated monolayer growth being observed over the temperature range 445–485 °C. The Fujitsu group³ achieved ALE growth using a low pressure MOCVD system with TMGa and AsH₃ being supplied as a fast pulsed gas stream from a jet nozzle, which

was found to be very effective in extending the monolayer limited growth window (460–550 °C). They called this particular setup pulsed-jet epitaxy (PJE).

II. CURRENT PROPOSED ALE MODELS FOR III-V COMPOUNDS

The ALE growth process is characterized by the self-limiting process, indicating the independence of the growth rate on the flux of the reactant gases. Several models were proposed and are summarized in Fig. 1.

(1) The selective adsorbate model¹¹ states that TMGa will not decompose on an atomic Ga-rich surface. It was supported by x-ray photoelectron spectroscopy (XPS) surface studies showing no carbon on TMGa dosed surfaces. However, XPS requires cooling and transport from the growth chamber to the XPS chamber, which is a significant change in the environment for the substrate. This model has been completely excluded by a study demonstrating TMGa decomposition on a Ga surface.¹²

(2) The adsorbate inhibition model will not allow decomposition of TMGa on a methylgallium species covered surface.¹³ It is supported by temperature programmed desorption (TPD) studies showing the lifetime of the methyl radicals under ultrahigh vacuum (UHV) conditions. This is not the complete picture, however, since at higher growth temperatures the methyl lifetimes are much too short to explain our ability to maintain ML/cycle growth.

(3) The flux balance model¹⁴ requires a balance to be maintained between desorbing monomethylgallium (MMGa) and adsorbing MMGa during the TMGa exposure. This

TABLE I. Summary of reported ALE growth conditions for GaAs with TMGa used at the gallium precursor.

Type of system pressure	Torr	Temperature range (°C)	Exposure time (s)	Reference
Vertical MOCVD rotating susceptibility	760	450–700	0.2–3/0.3 TMGa/AsH ₃	1
Vertical MOCVD rotating susceptibility	30	550–650	0.2–0.6/0.8/0.4/0.8 TMGa/purge/AsH ₃	2
Vertical chimney MOCVD	20	430–560	1–30/1–10 TMGa/AsH ₃	3
Vertical H ⁺ plasma MOCVD	20	430–500	3/2/2/2 TMGa/purge/AsH ₃ /purge	4
Horizontal MOCVD	100	500	3/2/4–8/2 TMGa/purge/AsH ₃ /purge	5
Horizontal MOCVD vent/run	100	$T < 460$	1/1/1/1 TMGa/purge/AsH ₃ /purge	6
Horizontal MOCVD vent/run	760	450	0.6/1.5/1.5/0 TMGa/halt/AsH ₃ /H ₂ /purge	7
Horizontal MOCVD	70	490–500	1/3/1/3 TMGa/purge/AsH ₃ /purge	8
UHV MOMBE		470	15–50/10/10/10 TMGa/evac/AsH ₃ /evac	9
UHV MOMBE		500	4/3/20/3 TMGa/evac/AsH ₃ /evac	10

seems to be an obvious requirement, but one which had been previously overlooked. There must be a compensation for desorbed TMGa from the surface, otherwise less than ML/cycle growth will result. However, the upper temperature limit of ALE growth has always been reported to be characterized by growth rates exceeding the ML/cycle; thus the flux balance model is not complete either.

None of these models completely explain the collection of ALE GaAs data published and presented in Table I. In this table, we listed reported ALE growth conditions for GaAs, using TMGa. From the table, a wide ALE temperature window was achieved by our group using the rotating substrate approach with provisions to reduce the gas phase reactions by shearing off the gas boundary layer. This window is wider than that achieved by other groups using near atmospheric pressure systems without any provision to reduce gas phase decomposition of TMGa. However, it seems that the UHV ALE approach where no gas phase decomposition occurs should yield a wider ALE window, which is not the case as shown in Table I. None of the available models specifically address why atmospheric pressure reactors can maintain ALE at temperatures far exceeding that of the UHV reactors,¹⁰ where the gas decomposition is insignificant. In the following, we will discuss the main gas phase and surface reactions and try to explain, based upon a flux balance of methyl radicals near the substrate surface, why the rotating substrate approach can sustain ALE at higher temperatures.

III. GAS PHASE REACTIONS

It is important to examine the gas phase decomposition of TMGa in H_2 for an understanding of ALE in a MOCVD reactor. The region above the substrate where the temperature is high enough for decomposition of TMGa to occur is the chemical boundary layer.¹⁵ Reactor conditions leading to the complete decomposition of TMGa in the gas phase represent the absolute limit of ALE in the MOCVD environment. Therefore, the characteristics of this chemical boundary layer and the time an incoming TMGa molecule spend in it are important reactor design issues.

The chemical boundary layer for TMGa established by the gas phase temperature at which it decomposes to Ga or other Ga species has been proposed to begin at 400 °C.¹⁶ The thermal profile in the hydrogen carrier for the TMGa above the hot substrate is therefore critical for ALE in the MOCVD reactor. Since the rotating susceptor in our reactor cuts into a relatively cool H_2 TMGa gas stream and then begins to heat this gaseous layer up to the substrate temperature, the thermal profile is transient. Estimates of these transient thermal profiles were made¹⁷ for substrate temperatures of 500, 600, and 700 °C by solving the heat conduction equation for a flat plate at a given substrate temperature, heating H_2 at a given height above the substrate (y) as a function of time. The boundary conditions are $T_{hydrogen} = T_{substrate}$ at interface ($y=0$) and $T_{hydrogen} = 0$ °C as $y \rightarrow \infty$. The transient profiles are shown in Fig. 2 for substrate temperatures of 500, 600, and 700 °C. Pertinent TMGa exposure times are included to indicate the

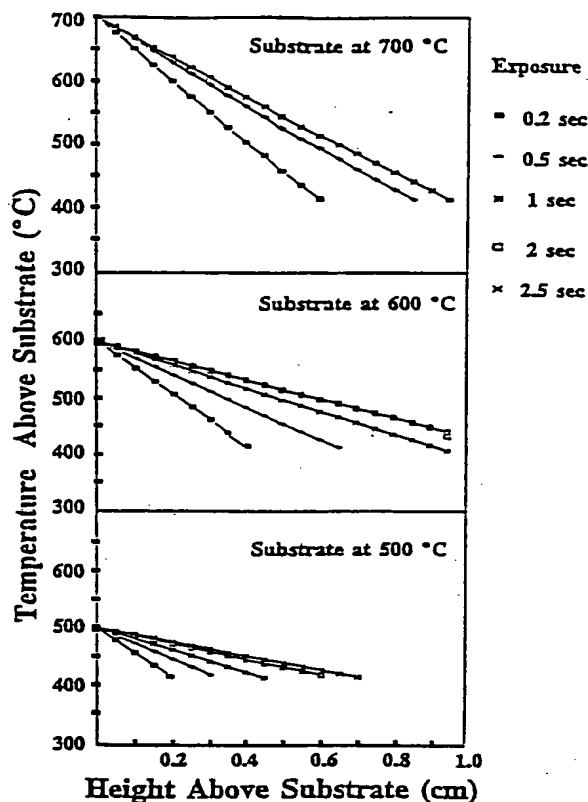


FIG. 2. Transient thermal profile in the H_2 above the hot substrate for a substrate temperature of 500, 600, and 700 °C for several TMGa exposure times.

strong dependence of the gas phase thermal profile on exposure time increments of fractions of a second at high substrate temperatures. At a substrate temperature of 500 °C, for example, and a 0.2 s exposure to TMGa the gas phase temperature $T_{hydrogen}$ is greater than 400 °C at a height of 0.25 cm above the substrate. As the substrate temperature is increased, the thermal profile expands and the chemical boundary layer gets thicker for the same exposure time to the TMGa/ H_2 stream. Another example is for a substrate temperature of 700 °C, as shown in Fig. 2. At this substrate temperature the thickness of the chemical boundary layer, where $T_{hydrogen} \geq 400$ °C, has increased to 0.65 cm for a 0.2 s TMGa exposure. Therefore, the volume where gas phase decomposition of the TMGa molecule is more likely has increased, and the self-limiting characteristic at higher growth temperatures exhibits a narrower (on the order of fractions of a second) window of exposure times to the TMGa/ H_2 stream. However, in most other MOCVD reactors the effective TMGa exposure is 1 s or longer, making high temperature ALE difficult, as shown in Table I.

From the gas phase decomposition of TMGa arguments alone, the ALE temperature range in the UHV reactor should extend beyond that of the MOCVD. On the contrary, the UHV data demonstrate a narrower ALE temperature window than MOCVD, and this has been explained by the limitations

established by the lifetime of surface-adsorbed CH_3 , referred to in the next section.

IV. METHYL RADICAL BALANCE MODEL

Based upon the system-dependent ALE temperature ranges and the above-mentioned gas phase and surface reactions, we propose the methyl radical balance as the self-limiting ALE mechanism. The surface must be stabilized with mono- or dimethylgallium molecules which are selective against chemisorption of TMGa. However, a balance between desorption of the methyl radicals from the monomethylgallium (MMGa) molecules at the surface and adsorption of methyls from the gas phase for the MOCVD type reactor is required during the TMGa exposure. The self-limiting ALE can be lost by two means, which may be a function of reactor type (pressure), growth temperature, and gas flux.

(1) If complete gas phase decomposition of incoming TMGa molecules leads to a surface covered with atomic gallium during the TMGa exposure, the surface of atomic gallium will not be self-limiting to further Ga or TMGa chemisorption.

(2) Methyls at the surface desorb faster than they can be replaced from the gaseous boundary layer, opening up sites of atomic Ga upon which TMGa can chemically adsorb. The desorption of MMGa is not a problem as long as there is a flux of TMGa to replace it, and as has been suggested, there is probably a balance of adsorbing MMGa and desorbing MMGa.¹² Thus the methyl radical balance model giving the condition for ALE self-limiting process can be simply stated as

$$\phi_{\text{gas}} > \phi_{\text{desorption}}$$

where ϕ_{gas} is the CH_3 flux impinging on the surface and is originated from the gas phase, and $\phi_{\text{desorption}}$ is the desorption rate for CH_3 from the $\text{Ga}(\text{CH}_3)$ adsorbed species.

For the high vacuum case, the self-limiting state is determined by the lifetime of methyl radicals adsorbed at the surface in the mono- or dimethylgallium. There is no boundary layer to provide a source of replacement of methyl radicals, and desorbing methyl radicals are not likely to return to the surface since their mean-free-path is large. If MMGa desorbs it can simply be replaced by the incoming flux of TMGa. If a methyl desorbs for the surface MMGa molecule, however, the resulting Ga atom is no longer self-limiting against the incoming TMGa flux and the growth rate exceeds ML/cycle. Thus, ALE in the UHV environment probably has a temperature limit from the surface kinetics that cannot be circumvented.

MOCVD type reactors, however, should be able to extend the ALE temperature range by decreasing the TMGa exposure time to minimize gas phase decomposition and increasing the TMGa flux to achieve surface saturation faster.

V. CURRENT CHALLENGES FACING THE ALE TECHNIQUE AND RECENT III-V COMPOUNDS RESULTS

The ALE technique has suffered from several shortcomings that we believe have delayed its potential application and discouraged many researchers.¹⁸ The first problem is very low growth rates, in some cases as low as $0.02 \mu\text{m}$. Some recent improvement in the growth rate was achieved and a growth rate of $\sim 0.1 \mu\text{m/h}$ was reported, which we believe to be discouragingly slow. The main reason for such a low growth rate is the commonly used approach based on exposure/purging each of the reactants with a vent/run manifold configuration.^{3,6} The finite gas reactor residence time and valve switching times will always lead to the growth of only a fraction of a $\mu\text{m/h}$. The approach we adopted in our laboratory¹ relies on rotating the substrate between the effluent source gas streams that are continuously flown through a specially designed vertical reactor. The growth rate will depend on the substrate rotation speeds. Growth rates in the range of $0.4\text{--}1 \mu\text{m/h}$ can be achieved with this approach.¹⁹ Such growth rates are comparable with the reported by MBE.

The second problem facing ALE of III-V compounds is the high carbon background in the ALE grown films. Recently,^{19,20} undoped GaAs with background electron concentrations in the high $10^{14}/\text{cm}^3$ to low $10^{15}/\text{cm}^3$ was grown in our laboratory. The liquid nitrogen temperature mobility was $\sim 30\,000 \text{ cm}^2/\text{V s}$, which is reasonably adequate for several devices. The device quality GaAs films were achieved by optimizing growth conditions such as growth temperature, flux of reactants and exposure times. Thus, we believe that at least for GaAs the ALE technique can provide films with convenient growth rates and good electrical properties.

Another problem facing ALE is the synthesis of ternary alloys such as AlGaAs and InGaAs required for heterostructures with different binary compounds. The problem with ternary alloys is the lack of compatible group III precursor that will adhere to the self-limiting process at the same growth temperature.²¹

Most of these difficulties have been addressed successfully using ALE growth system that relies on the rotating substrate approach.^{19,20} Recent achievements in the III-compound area can be summarized as follows.

- (1) ALE with growth rate $\geq 2 \mu\text{m/h}$.²²
- (2) ALE of device quality ternary alloys such as AlGaAs and InGaP.^{23,24}
- (3) ALE of several devices such as planar-doped field effect transistor,²⁵ heterojunction bipolar transistor,²⁶ storage capacitance,²⁷ and resonant tunnelling diodes.²⁸

VI. ALE OF SILICON

For II-VI or III-V compound semiconductors, the ALE growth has been achieved by sequential injections of source gases containing respective components of semiconductor whose heterogeneous reactivities change with surface conditions.²⁹ On the other hand, group IV semiconductor are constructed with only one component. Therefore, ALE of group IV element consists of the two processes as follows.

The first step of ALE is the monolayer adsorption of partially decomposed source gas molecules over the clean surface. The adsorbate is constructed with a Si (or Ge) atom and another kind of atoms (or groups) bonded with Si (or Ge), such as SiCl_x or $\text{Ge}(\text{CH}_3)_x$. The Si (or Ge) atoms in adsorbates terminate the surface dangling bonds and make a grown monolayer, and the atoms (or group) such as Cl (or CH_3) cover the newly grown layer surface. Therefore, when whole, the surface is covered by the adsorbates, monolayer growth is achieved. Successive source gas cannot be adsorbed chemically because the surface is completely covered and there are no dangling bonds. As a result, the growth is limited to 1 ML, that is, the self-limiting growth is achieved. The second step is the removal of the surface-terminating atoms (or groups) in some way.

Although many studies on the ALE of compound semiconductors were reported after the proposal of ALE in the 1970s,²⁹ the history of Si ALE has started in the last few years. First, successful ALE of Si has been reported by Nishizawa *et al.*³⁰ using dichlorosilane (SiH_2Cl_2) as a source gas and hydrogen (H_2) as a reducer gas. SiH_2Cl_2 was decomposed into SiCl_x , and SiCl_x is adsorbed on the clean Si surface. The recovery of the clean surface was made by the reduction of surface-terminating Cl atoms by H_2 to HCl. The growth temperature was, however, more than 815 °C for (100)Si and more than 890 °C for (111)Si. This temperature is too high to fabricate new materials and structures such as Si-Ge heterojunction or superlattices because of the diffusion of Si and Ge.

Two possible ways to lower the substrate temperature exist. The first way is the use of higher silane as a source gas, where surface-terminating atoms are H atoms instead of Cl atoms. H atoms terminating the Si surface are well known to be thermally desorbed from the Si surface at ~600 °C which is much lower than for Cl atoms.³¹ Therefore, repetition of the injection of higher silane as a source gas and heating up the substrate for thermal desorption of H atoms can result in ALE. The second method is to use atomic H to reduce the surface terminating Cl atoms. The two approaches will be discussed in detail in the following sections.

VII. UV-PHOTOASSISTED SI ALE

This approach was developed by Greene and co-workers.³² This approach relies on the self-limiting adsorption of Si_2H_6 at temperature (T_s) below the H_2 desorption temperature, followed by a rapid photothermal heating with an excimer laser pulse to desorb the surface hydrogen. Results³³ can be summarized as follows. Figure 3 shows the film growth rate R as a function of the steady-state substrate temperature T_s with and without pulsed laser irradiation during each deposition cycle. The peak pressure during the 1 s Si_2H_6 exposures was 1.5 Torr, sufficient to reach surface saturation, as shown below, in all experiments. The maximum KrF laser energy density E_{max} at the sample surface in the irradiation experiments was decreased from 470 to 250 mJ cm^{-2} as T_s was increased from 130 to 550 °C. The energy density window ΔE over which R was found to be constant for a given, $T_s = 150 \text{ mJ cm}^{-2}$. R in Fig. 3 is plotted in units of ML per growth cycle, where 1 ML in the [001]

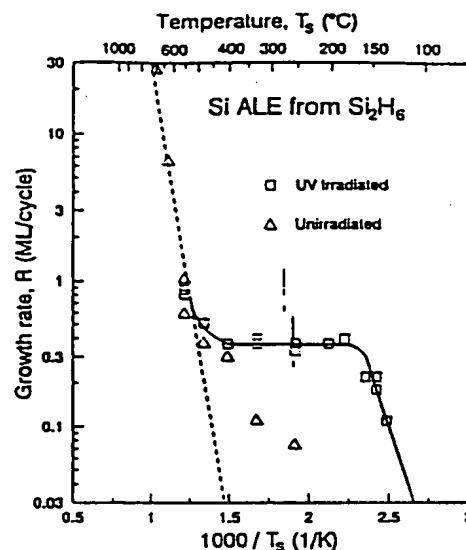


FIG. 3. Si growth rate R as a function of substrate temperature T_s .

direction is taken to be $6.8 \times 10^{14} \text{ cm}^{-2}$ corresponding to a thickness of 0.136 nm. For the unirradiated films, R varied exponentially with $-1/T_s$ at $T_s \geq 550 \text{ °C}$ yielding an apparent activation energy of 1.2 eV. At lower temperatures, the slope is reduced, and no measurable growth occurred at T_s below 200 °C. Films deposited with $T_s \geq 625 \text{ °C}$ were smooth, high-quality epitaxial layers, as judged by reflection high-energy electron diffraction (RHEED), while films deposited at lower temperatures exhibited three-dimensional RHEED patterns with increased diffuse background intensity indicative of residual disorder.

In contrast, all films deposited at low temperatures with pulsed UV laser irradiation were smooth and well ordered, as judged by both RHEED and transmission electron microscopy, and exhibited much higher deposition rates at $T_s \leq 400 \text{ °C}$.³³ In fact, at $T_s = 250 \text{ °C}$, R increased by more than an order of magnitude in the presence of laser irradiation. Moreover, there is a range in growth temperatures between ~180 and 400 °C over which R is independent of T_s , and deposition proceeds by a kinetically self-limited ALE mechanism with no apparent activation barrier. Varying the number of laser pulses per cycle from 10 to 50 also had no effect on R which remained constant at ~0.4 ML/cycle. For $T_s > 400 \text{ °C}$, the growth rate of the laser irradiated films increases with increasing T_s , as deposition due to thermal pyrolysis begins to compete with ALE. At $T_s < 180 \text{ °C}$, R decreases with an apparent activation energy of ~0.5 eV.

The film growth rate as a function of the peak Si_2H_6 pressure P during a 1 s exposure with $T_s = 250 \text{ °C}$, $E = 400 \text{ mJ cm}^{-2}$, and $n_p = 10$ pulses is shown in Fig. 4. Measurable R values were obtained for $P \geq 0.1 \text{ mTorr}$ and saturation was observed at $P_{\text{sat}} \approx 1.5 \text{ mTorr}$ with $R \approx 0.4 \text{ ML/cycle}$. These results are further evidence of a self-limited kinetic growth mechanism. The Si_2H_6 saturation exposure in Fig. 4 is in good agreement with the exposure required to obtain a satu-

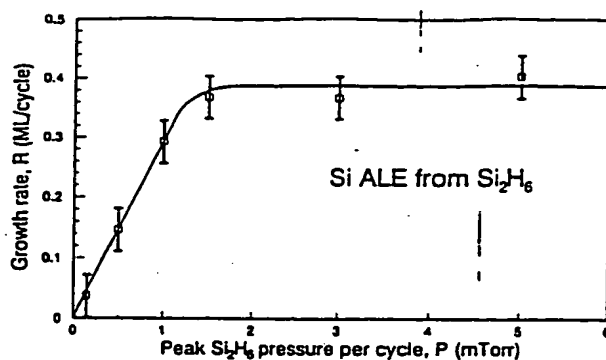


FIG. 4. Si growth rate R as a function of the maximum chamber pressure P during the Si_2H_6 gas pulse. The film growth temperature T_s was 250°C , the KrF irradiation energy density E was 400 mJ cm^{-2} , and the number of laser pulses per gas pulse n_p was 10.

rated $(1\times 1)::2\text{H}$ dihydride surface during Si_2H_6 adsorption experiments at room temperature.³⁴ However, the incident flux, and hence the time of exposure, in the latter case was ~ 4 orders of magnitude lower than that employed in the present growth kinetics experiments.

The ALE growth rate was also found to be constant for a wide range in incident UV energy densities. While ΔE remained $\sim 150\text{ mJ cm}^{-2}$, E_{max} had to be decreased as the substrate temperature increased in order to achieve the same peak temperatures. In all cases, the laser-induced temperature was sufficient to cause complete removal of the hydrogen but less than that required for melting. One-dimensional heat-flow calculations, based upon optical absorption and incorporating temperature-dependent thermal parameters,³⁵ were used to estimate the melting threshold as a function of T_s and E . For 22 ns KrF irradiation, the $1/e$ absorption depth is $\sim 5.6\text{ nm}$ and the threshold energy density for melting was found to vary from 480 to 410 mJ cm^{-2} as T_s was increased from 250 to 400°C . At $T_s=250^\circ\text{C}$, ALE growth with $R\sim 0.4\text{ ML}$ per growth cycle was obtained for $300 < E < 470\text{ mJ cm}^{-2}$, while for $T_s=400^\circ\text{C}$ the measured useable E range was 220–365 mJ cm^{-2} .

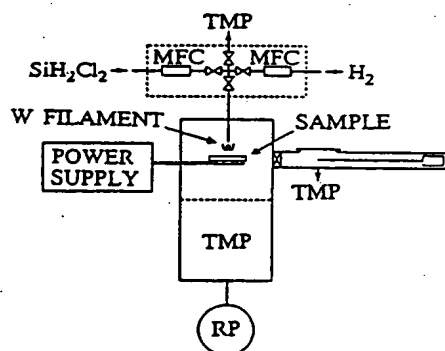


FIG. 5. Schematic view of ALE system using SiH_2Cl_2 and atomic H.

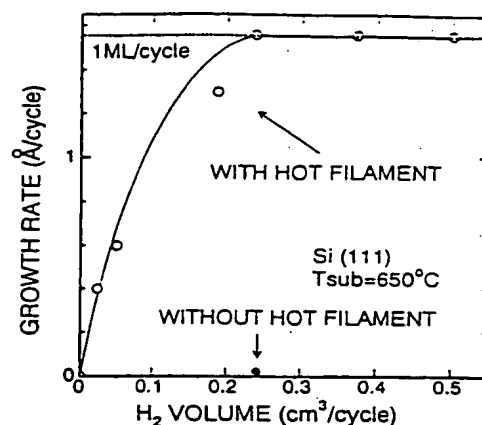


FIG. 6. Thickness per unit ALE cycle as a function of the H_2 gas volume within an ALE cycle.

VIII. ALE OF SILICON USING ATOMIC HYDROGEN

The second way to is to use SiH_2Cl_2 with a reducer much more active than H_2 . The use of atomic hydrogen (H) as a reducer in Si ALE growth was reported.³⁶ H atoms are able to be created easily and plasma-freely by decomposition of H_2 using an incandescent tungsten filament.^{37,38} Si ALE growth by sequential exposures into SiH_2Cl_2 as a source gas and H as a reducer gas was successfully reported³⁶ and ideal monolayer growth per cycle has been demonstrated at 540°C . The ALE system used in their experiment was assembled as shown in Fig. 5. Figure 6 shows the growth rate as a function of the injected H_2 gas volume per cycle with the substrate temperature of 650°C .³⁶ When the filament was not used, no growth occurred, however, with the filament, the growth rate increased with H_2 volume. This means that H atoms were effective for Cl reduction at low temperatures. Reaching 1 ML/cycle, the growth rate was saturated, i.e., the ALE growth was achieved in spite of very low substrate

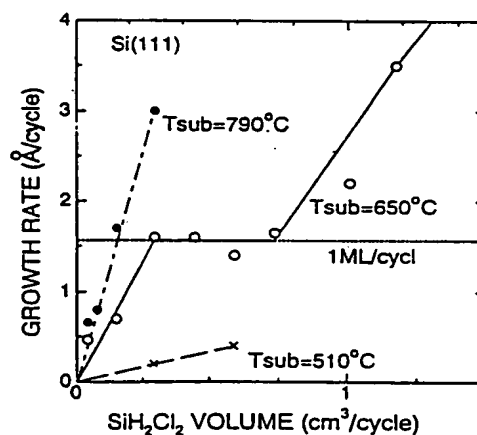


FIG. 7. Thickness per unit ALE cycle as a function of the SiH_2Cl_2 gas volume within an ALE cycle.

temperatures. Figure 7 shows the growth rate as a function of the SiH_2Cl_2 gas volume at the substrate temperatures of 520, 650, and 790 °C.³⁶ Only the SiH_2Cl_2 gas flow rate was changed and other parameters were kept constant. At 520 °C, the growth rate increased with the gas volume, but was less than 1 ML/cycle. At 650 °C, the growth rate increased up to 1 ML/cycle with the gas volume and is saturated. In this saturation region, ALE growth was achieved. At 790 °C, the growth rate increased over 1 ML/cycle with no clear saturation.

IX. CONCLUSIONS

ALE growth of III-V and silicon has been outlined. Self-limited processes have been observed in both cases. ALE of III-V compounds has produced device quality films and state-of-the-art devices. The quality of ALE Si films is not yet known.

ACKNOWLEDGMENTS

The authors would like to thank ONR/SDIO, NSF, and NREL for partial support for this work.

- ¹S. M. Bedair, M. A. Tischler, T. Katsuyami and N. A. El-Masry, *Appl. Phys. Lett.* **47**, 51 (1985).
- ²P. C. Colter, S. A. Hussien, A. Dip, M. U. Erdogan, W. M. Duncan, and S. M. Bedair, *Appl. Phys. Lett.* **59**, 1440 (1991).
- ³M. Ozeki, K. Mochizuki, N. Ohtsuka, and K. Kodama, *J. Vac. Sci. Technol.* **5**, 1184 (1987).
- ⁴M. de Keijser and C. van Opdorp, *Appl. Phys. Lett.* **58**, 1184 (1991).
- ⁵A. Usui and H. Watanabe, Third International Conference on Modulated Semiconductor Structures, Montpellier, France, 1987 (unpublished).
- ⁶S. DenBaars, A. Hariz, C. Beyler, B. Maa, Q. Chen, and P. Dapkus, *Mater. Res. Soc. Symp. Proc.* **102**, 527 (1988).
- ⁷E. Colas, R. Bhat, and B. Skromme, *Appl. Phys. Lett.* **55**, 2769 (1989).
- ⁸H. Yokoyama, M. Shinohara, and N. Inoue, *Appl. Phys. Lett.* **59**, 2148 (1991).
- ⁹A. Watanabe, T. Isu, M. Hata, T. Kamijoh, and Y. Katayama, *Jpn. J. Appl. Phys.* **L1080** (1989).
- ¹⁰J. Nishizawa, H. Abe, and T. Kurabayashi, *J. Electrochem. Soc.* **132**, 1197 (1985).
- ¹¹K. Kodama, M. Ozeki, K. Mochizuki, and N. Ohtsuka, *Appl. Phys. Lett.* **54**, 656 (1989).
- ¹²J. R. Creighton, K. R. Lykke, V. A. Shamamian, and B. D. Kay, *Appl. Phys. Lett.* **57**, 279 (1990).
- ¹³J. Nishizawa and T. Kurabayashi, *J. Cryst. Growth* **93**, 98 (1988).
- ¹⁴*Chemical Perspectives of Microelectronic Materials II*, edited by M. L. Yu, U. Memmert, N. I. Buchan, and T. F. Keuch, L. V. Interrante, K. F. Jensen, L. H. Dubois, and M. E. Gross (Materials Research Society, Pittsburgh, PA, 1991), Vol. 204.
- ¹⁵M. H. J. M. de Croon and L. J. Giling, *J. Electrochem. Soc.* **137**, 2867 (1990).
- ¹⁶J. Nishizawa and T. Kurabayashi, *J. Electrochem. Soc.* **130**, 413 (1983).
- ¹⁷K. G. Reid, A. F. Myers, N. A. El-Masry, and S. M. Bedair, *Thin Solid Films* **225**, 59 (1993).
- ¹⁸S. M. Bedair, *Acta Polytech. Scand.* **195**, 17 (1990).
- ¹⁹P. C. Colter, S. A. Hussien, A. Dip, M. U. Erdogan, W. M. Duncan, and S. M. Bedair, *Appl. Phys. Lett.* **59**, 12 (1991).
- ²⁰J. R. Gong, P. Colter, D. Jung, S. Hussien, C. Parker, A. Dip, W. Duncan, and S. M. Bedair, *J. Cryst. Growth*, **107**, 83 (1990).
- ²¹W. Jeong, E. Menu, and P. D. Dapkus, *Appl. Phys. Lett.* **55**, 244 (1989).
- ²²A. Dip, G. Eldallal, P. Colter, and S. M. Bedair, *Appl. Phys. Lett.* **62**, 2378 (1993).
- ²³A. Dip, G. Eldallal, P. Colter, and S. M. Bedair, *Thin Solid Films* **225**, 109 (1993).
- ²⁴B. McDermott, N. El-Masry, F. Hyuga, and S. M. Bedair, *J. Cryst. Growth* **107**, 96 (1991).
- ²⁵M. Hashemi, B. McDermott, U. Meshra, J. Ramdani, A. Morris, J. Hauser, and S. M. Bedair, *IEEE Trans. Electron Device Lett.* **EDL-12**, 258 (1991).
- ²⁶T. Henderson, B. Bayraktaroglu, S. Hussien, A. Dip, P. Colter, and S. M. Bedair, *Electron Lett.* **27**, 692 (1991).
- ²⁷S. M. Bedair, B. McDermott, K. Reid, P. Neudeck, J. Cooper, and M. Melloch, *IEEE Trans. Electron Device Lett.* **EDL-11**, 261 (1990).
- ²⁸A. C. Seabaugh, J. H. Luscombe, J. N. Randall, P. C. Colter, A. Dip, G. Eldallal, and S. M. Bedair, *Thin Solid Films* **225**, 99 (1993).
- ²⁹T. Suntola and M. J. Antson, U. S. Patent No. 4058430 (1977).
- ³⁰J. Nishizawa, K. Aoki, S. Suzuki, and K. Kikuchi, *J. Cryst. Growth* **99**, 502 (1990).
- ³¹G. Schulze and M. Henzler, *Surf. Sci.* **124**, 336 (1983).
- ³²Y. Suda, L. Lubben, T. Motooka, and J. E. Greene, *J. Vac. Sci. Technol. B* **7**, 1171 (1990).
- ³³D. Lubben, R. Tsu, T. R. Bramblett, and J. E. Greene, *Mater. Res. Soc. Symp. Proc.* **22**, 177 (1991).
- ³⁴Y. Suda, D. Lubben, T. Motooka, and J. E. Greene, *J. Vac. Sci. Technol. A* **8**, 61 (1990).
- ³⁵K. Suzuki, D. Lubben, and J. E. Greene, *J. Appl. Phys.* **58**, 979 (1985).
- ³⁶S. Imai, T. Iizuka, O. Suguira, and M. Matsura, *Thin Solid Films* **225**, 168 (1993).
- ³⁷I. Langmuir, *J. Amer. Chem. Soc.* **34**, 860 (1912).
- ³⁸O. Sugiura, T. Shiraiwa, H. Kanoh, and M. Matsumura, *Mater. Res. Soc. Symp. Proc.* **258** (1992).